EFFECTS OF STOICHIOMETRY AND EPOXY MOLECULAR MASS ON WETTABILITY AND INTERFACIAL MICROSTRUCTURES OF AMINE-CURED EPOXIES

by

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INTRODUCTION

Understanding the relationships between network structure and surface and interface properties of epoxy resins is a subject of great interest in many applications including adhesives, coatings and fiber-reinforced composites. However, this subject has not been fully investigated partly because of the spatial resolution limitation of traditional surface analytical techniques. Atomic force microscopy (AFM) is increasingly used for studying sub-micrometer features of polymer surfaces and interfaces. In this study, the influence of epoxy equivalent mass and epoxy/amine stoichiometry on surface and interface microstructures and wetting properties of amine-cured epoxy is investigated using AFM and contact angle measurements.

EXPERIMENTAL**

The epoxy resins were based on a homologous series of diglycidyl ether of bisphenol A. Six different epoxy equivalent masses (EEM) (molecular mass divided by number of epoxide groups) ranging from 190 g/mol to 3050 g/mol were used. The curing agent was a triamine based on propylene oxide. For each epoxy-amine system, both thin (< 50 nm) and thick films (~150 μm) were prepared by mixing the epoxy resin with three different amounts of the curing agent to provide epoxide:NH ratios of 0.75, 1.0 and 1.25. The substrates were silicon wafer and polished steel. Both substrates were cleaned thoroughly with detergent, rinsed repeatedly with distilled water followed with methanol, and dried with hot air.

Thin films were prepared from 0.08 % solutions of epoxy-amine in solvent, which was a mixture of 80 % of toluene and 20 % of ethylene glycol monobutyl ether (all percentages are based on material mass). After mixing the resin and curing agent at appropriate stoichiometry, the solutions were cast on the substrate using a spin coater. Thick films were prepared by mixing solutions of epoxy resin in 50 % toluene/50 % ethylene glycol monobutyl ether solvent with the curing agent. The mixtures were degassed for three h before applied to the substrates by draw down technique. The curing consisted of 24 h at ambient condition (24 ^{o}C and 45 % relative humidity), followed by post curing at 100 °C in an air-circulating oven for 1 h. Cross sections of thick film-coated steel samples were made following the usual procedures for preparing cross sections for microscopic study. Strips of coated steel were imbedded in a molding compound, and cross sections were obtained by cutting the embedded samples with a diamond saw followed with several polishing steps. Final polish was with a 0.25 μm diamond paste.

AFM measurements were performed using the Dimension 3100 Digital Instruments under ambient conditions. Both AFM topographic and phase images were taken in the tapping mode. For most of the images, a set point amplitude less than 50 % of the free amplitude was used. Silicon tips having a drive frequency of about 300 kHz and a radius of approximately 5 nm were used.

Both advancing and receding contact angles of water, methylene iodide and formamide on thick film samples were measured using the sessile drop method. Eight measurements were taken for each liquid on each epoxy-amine system. Surface free energy components and acid-base parameters were estimated by the three-liquid method of Good [1]. The polar and nonpolar components of each surface were also calculated via both geometric mean and harmonic mean methods [2].

RESULTS AND DISCUSSION

Wetting Properties.

The principal reactions which occur during curing of a mixture of an epoxy and a trifunctional aliphatic amine involve the reaction of the amine group with the epoxide to produce a three-dimensional crosslinked network, where the epoxy chains are linked by the amine molecules. The chain length between crosslinks increases (i.e, decreased crosslink density) with increasing EEM. Since the reaction between each amine hydrogen and an epoxide group produces one OH group on each epoxy chain, the number of OH group per unit volume increases with a decrease of the EEM. Thus, an amine-cured epoxy system from a lower molecular mass epoxy contains a greater number of OH groups per unit volume of the cured structure than that of a higher molecular mass epoxy. That is, the bulk polarity of an amine-cured epoxy should increase with a decrease of the EEM.

Results of advancing contact angle and surface free energy and its components estimated from the harmonic mean method are summarized in Table 1. Additional results on surface free energy and its components estimated using the other two methods, receding angles and the corresponding surface free energy component values, work of adhesion calculated from the three methods, and acid-base parameters calculated from the Good method show the same behavior as given in Table 1. That is, a change in the equivalent mass of the epoxy resin does not appear to have

a strong or trendy effect on the wetting properties of amine-cured epoxy films.

Epoxy Equiv. Mass (g/mol)	θ_w degree	θ_{mi} degree	Surface free energy components (mJ/m²)		
			γ_s^d	γ_s^p	γ_s
190	63.1±0.7	40.6±1.3	36.88	16.97	53.85
255	59.3±1.6	32.1±4.2	40.40	18.05	58.45
500	65.7±1.4	41.9±1.8	36.32	15.80	52.13
900	58.5±1.5	44.1±1.3	35.28	19.74	55.03
2250	61.7±1.9	44.1±1.1	35.30	18.08	53.39
3050	62.3±1.6	44.4±1.2	35.17	17.81	52.98

θ_w : water contact angle; θ_{mi}: methylene iodine contact angle; γ_s^d , γ_s^p , γ_s : Nonpolar, polar and total surface free energy, respectively. Values after the ± sign indicate one standard deviation.

AFM Results

Representative AFM images of each amine/epoxy sample thin films cured in ambient air are displayed in Figures 1a to 1d. Although the topographic (height) image (Figure 1a) shows some features of the surface, the microstructure is better seen in the phase image (Figure 1b), which shows bright, nodular domains having dimensions ranging from 30 nm to 70 nm surrounded by a dark matrix. The nodular domains are seen as depression in the 3-d topographic image (Figure 1c). The bright domains in the phase image have been interpreted as due to a mechanically harder area and the bright surrounding region as due to more compliant material [3,4]. The nodular microstructure observed in Figure 1 is true for all samples and is consistent with previous observations [5,6], which showed that amine-cured epoxy is an heterogeneous material consisting of highly crosslinked regions surrounded by less crosslinked, low molecular mass material. Such inhomogeneous structure is generated during the film formation because some unreacted and partially-polymerized materials are unable to merge into the homogeneous structure and remain at the periphery of the network units [7].

In addition to the film microstructure, Figures 1a and 1b also reveal the presence of numerous large particles having sizes ranging from 40 nm to 800 nm on the surface. This feature, whose 3-d image is displayed in Figure 1d, is probably due to the carbonate salts formed by the side reaction between an amine and CO_2 in the air. These salts have been found responsible for the intercoat adhesion loss of amine-cured epoxy coatings [8]. The size and number of these hydrophilic particles on the surface should have an effect on the wettability of an amine-cured epoxy.

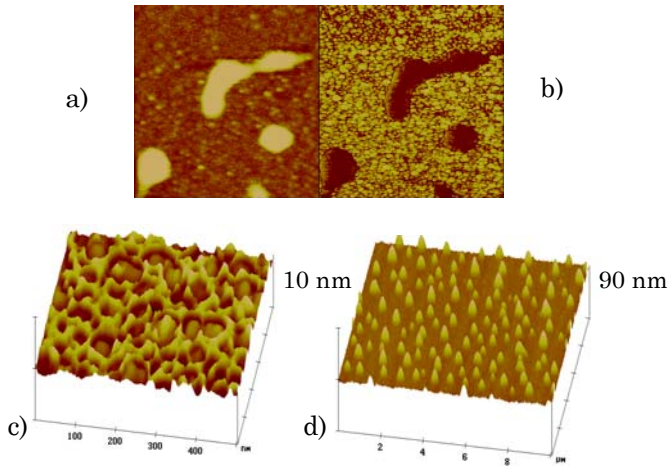


Figure 1. Typical AFM images of amine-cured epoxy films: a) 2-D topographic image, b) phase image. Contrast variation from black to white: 10 nm (topographic image), 120° (phase image) c) 3-D topographic image (500 nm ×500 nm), and d) low magnification 3-D image (10 µm × 10 µm) showing large particles on sample surfaces. Epoxy equivalent mass: 500g, stoichiometry:1/1

The microstructure of the film surface in contact with the substrate was also investigated. In this case, a thick film was removed from the substrate and the interior surface was imaged. Figures 2a and 2b display both the height and phase images of surfaces exposed to the air and the silicon substrate, respectively. The surface in contact with the substrate has a well-defined microstructure, which exhibits larger nodules than those from the air surface. The larger-size nodules of the film/substrate interface, as compared to the film/air interface, suggest that crosslinking at the former was probably more efficient than that at the latter. Further, the distinct clarity difference of features between the film/air interface and the film/substrate interface indicates that both chemical composition and phase separation at the two interfaces are quite different.

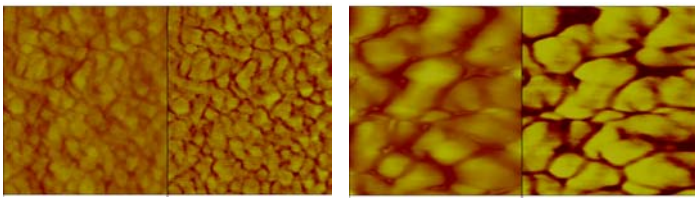
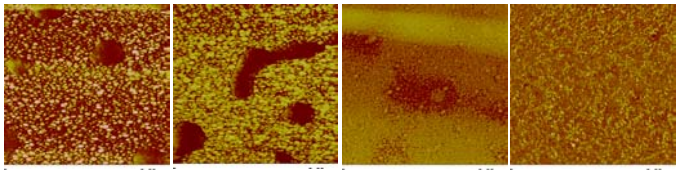


Figure 2. 500 nm × 500 nm topographic and phase AFM images of a approximately 150 µm thick epoxy film: a) film/air interface, and b) film/silicon interface; 3050 g/mol, epoxy/amine: 1/1. In both a) and b), topographic image is on the left and phase image is on the right. Contrast variation from black to white; on the topographic image: a) 5 nm, b) 10 nm; on the phase image: a) 90°, b)100°.

Both the amine-CO_2 side reactions, which result in incomplete crosslinking on the air surface, and the amine preferentially adsorbed on the substrate surface [9], which facilitates the curing conversion, may partially explain for

the different microstructures observed in Figure 2a and Figure 2b.

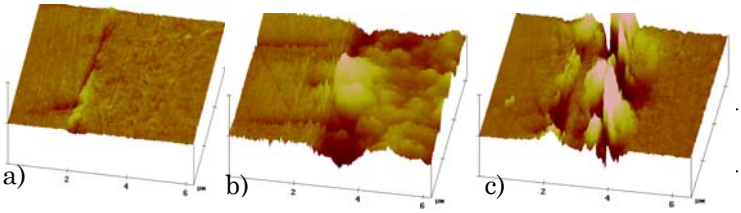
The effects of EEM on surface microstructure and interphasial characteristics of amine-cured epoxy are shown in Figures 3 and Figure 4, respectively. The size of the nodules in the surface images appears to decrease with increasing EEM, suggesting that a more extensive crosslinking had occurred in the domains of the low EEM material than that of the high EEM.



a) b) c) d)

Figure 3. AFM 2 μm × 2μm phase images of amine-cured epoxy for different epoxy molecular masses: a) 255 g/mol, b) 500 g/mol, c) 900 g/mol, 3050 g/mol; Epoxy/amine: 1/1.

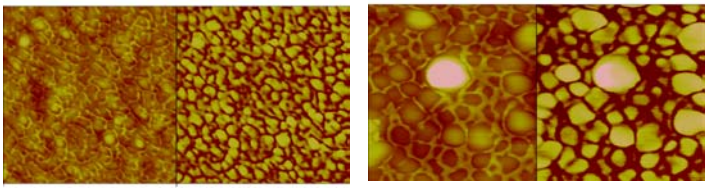
Figure 4 shows 3-d topographic images of cross sections of thick films of amine-cured epoxy prepared from different epoxy equivalent masses coated on polished steel substrates. In these figures, the steel substrate is on the left and the cured epoxy material is on the right of the rough interphase region, which is defined as the rough area between the epoxy and the steel substrate. The large difference between the peaks and valleys in the interphase region were induced by a mechanical property that is different from either material. It appears that the width of the interphase region, which ranges from approximately 0.1 μm for the 190 g/mol to approximately 2 μm for the 3050 g/mol, increases with an increase in the EEM.



a) b) c)

Figure 4. AFM 3-d topographic images of cross sections of amine cured epoxy on steel for different epoxy molecular masses: a) 190 g/mol, b) 500 g/mol, 3050 g/mol; Epoxy/amine: 1/1. Height contrast variation between black and white: 250 nm.

Figure 5 displays an example of the effects of stoichiometry on the film/air interface microstructure of an amine-cured epoxy system. These are 500 nm x 500 nm scans of topographic and phase images of the 190 g/mol EEM samples at epoxy/amine of 1/1 and 1.25/1. Figure 5 shows a higher percentage of the dark area surrounding the nodular domains for the amine-deficient samples than that of the 1/1 sample, suggesting that a larger amount of softer material is present in these films. Further, the nodule aspect ratio of the amine deficient samples appear to be lower than that of the 1/1 sample



a) b)

Figure 5: Effect of stoichiometry on film/air interface microstructure; AFM 500nm×500nm images of a) epoxy/amine:1/1; b) epoxy/amine: 1.25/1 (in both a and b: left is topographic image and right is phase image). Contrast variation from black to white: on the topographic image: a) and b) 10nm.; on the phase image: a) 90°, b) 120°

CONCLUSIONS

The surface microstructure of an amine-cured epoxy exposed to air is quite different from that of the surface in contact with a silicon substrate. The substrate-contact surface microstructure is clearly defined, which consists of larger nodular domains as compared to those at the film/air surface. This result suggests that a difference in both chemical composition and phase separation exists at the two interfaces. The nodule size decreases and the cured epoxy/steel interphasial width increases with an increase in the epoxy molecular mass. On the other hand, epoxy molecular mass does not seem to affect the wettability of amine-cured epoxies.

***Certain commercial product or equipment is described to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that it is necessarily the best available for the purpose.*

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